crystals. Recrystallization from the minimum amount of water gave 8.0 g. of white crystals (47.5%), which melted at 183.5–184°. The loss encountered in the recrystallization was due to the inclusion of excess sodium acetate in the crude precipitate.

Anal. Calcd. for $C_7H_7ON_2S$: N, 8.28. Found: N, 8.23.

5-Acetamido-2-thenaldoxime.—This aldehyde gives an immediate deep violet precipitate with 2,4-dinitrophenylhydrazine in alcohol, but the melting point of this derivative was above 300° and it was too insoluble to be readily crystallized. The oxime was readily formed by the usual procedure and crystallized in glistening white needles which, even after repeated crystallization from water, had a broad melting range, 198–202°. This may be due to the presence of *syn* and *anti* isomers, since the analysis was satisfactory.

Anal. Calcd. for $C_7H_8O_2N_2S$: N, 15.21. Found: N, 15.35.

5-Acetamido-2-thenoic Acid.—Three-tenths of a gram of 5-acetamido-2-thenaldehyde (0.00177 mole) was dissolved in 60 ml. of stock Fehling solution[12] (30 ml. of solution I and 30 ml. of solution II) and 100 ml. of water and the blue solution allowed to stand at room temperature for three days. The red precipitate of cuprous oxide was then filtered off, the aqueous solution concentrated to approximately 50 ml. and cooled to give 0.32 g. (quantitative yield) of white crystalline 5-acetamido-2-thenoic acid, which when recrystallized from hot water melted at 271–272°, as previously reported.[13]

Anal. Calcd. for $C_7H_7NO_3S$: neut. equiv., 185. Found: neut. equiv., 182.

p-**Dimethylaminobenzaldehyde.**[14]—Fifty-one grams (0.34 mole) of phosphorus oxychloride was added dropwise with stirring and cooling to 88.0 g. (1.2 moles) of dimethylformamide contained in a 500-ml. three-necked flask equipped with a reflux condenser, drying tube, stirrer, and dropping funnel. To this mixture was added dropwise with stirring 40.0 g. (0.34 mole) of technical dimethylaniline, after which the solution was heated with stirring on a steam-bath for two hours. The mixture was poured over ice and neutralized by dropwise addition of aqueous sodium acetate with vigorous stirring. Any excessive increase in temperature of the aqueous solution during neutralization led to the formation of greenish-blue dyestuffs which could not be removed from the product by recrystallization or acidification and reprecipitation by alkali. White crystalline *p*-dimethylaminobenzaldehyde which weighed 34.8 g. (70.5%), was obtained from the neutral solution after standing overnight in a refrigerator. The product was essentially pure as it precipitated from the reaction mixture.

9-Anthraldehyde.—In a 1-l. three-necked flask equipped with a reflux condenser, drying tube and stirrer was placed 18.0 g. (0.104 mole) of anthracene (m.p. > 215°), 16.0 g. (0.22 mole) of technical dimethylformamide, 28.0 g. (0.118 mole) of phosphorus oxychloride and 20 cc. of *o*-dichlorobenzene. The suspension was stirred and heated on a steam-bath for 30 minutes to complete solution, after which the heating was continued for an additional 90 minutes. The cool reaction solution was then neutralized with aqueous sodium acetate and diluted with water to a volume of 2 liters. After standing overnight in a refrigerator the yellow precipitate was filtered from the mother liquor and recrystallized from 50 ml. of glacial acetic acid. Washing the acetic acid from the resulting crystals with a small amount of cold methanol gave 13.0 g. (62.5%) of beautiful yellow needles of 9-anthraldehyde. An attempt to use excess dimethylformamide to replace the *o*-dichlorobenzene solvent resulted in a lower yield of aldehyde which was more difficult to purify. The *o*-dichlorobenzene held the unreacted anthracene in solution at the point of neutralization and prevented contamination of the product.

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(12) L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., New York, N. Y., 1941, p. 86.

(13) H. D. Hartough, "Thiophene and its Derivatives," Interscience Publishers, Inc., New York, N. Y., 1952, p. 380.

(14) The preparation of this compound by the DMF procedure is not original (British Patent 607,920 (1948); *C. A.*, **43**, 2232 (1949)) but is repeated for convenience.

Acidity and Infrared Absorption of Fluorinated Alcohols

By Albert L. Henne and William C. Francis

It is now firmly established that the ionization constant of alcohols perfluorinated in the α-position is of the order of magnitude of $K_i = 10^{-12}$. Specifically, we have reported 4.0×10^{-12} for CF_3-CH_2OH,[1] and 1.2×10^{-11} and 4.1×10^{-12} for the first and second constants of $HOCH_2CF_2CF_2$-CH_2OH,[2] in good agreement with similar results reported from other laboratories.[3] Perfluorinated primary alcohols are thus about 10^6 times more acid than their unfluorinated analogs, and we have wondered whether this increase might be about doubled in secondary alcohols, and perhaps almost tripled in tertiary alcohols. This was found not to be the case. Specifically, ionization constants were measured as 4.3×10^{-12} for $C_3F_7CH_2OH$, 4.3×10^{-12} for $C_3F_7CH(OH)C_3H_7$ and 2.2×10^{-11} for $C_3F_7CH(OH)C_3F_7$. The bulk of the inductive effect is thus exercised by the first fluorinated group, and we can now predict that perfluorinated tertiary alcohols will prove comparable to phenol in acidity, at best.[4]

The three alcohols were prepared as follows: $C_3F_7CH_2OH$ by reduction of the acid with lithium aluminum hydride, $C_3F_7CH(OH)C_3F_7$ by reduction of the ketone with the same reagent, and C_3F_7-$CH(OH)C_3H_7$ by condensation of C_3F_7MgI with butyraldehyde; the preparations of C_3F_7MgI, $C_3F_7COC_3F_7$ and $C_3F_7CH(OH)C_3H_7$ are given in an accompanying paper.[5]

The ionization constants were determined by glass electrode measurements of the *p*H at the half-equivalence point in 50% aqueous methanol, using tenth normal sodium hydroxide in the same solvent.

Perfluorinated secondary heptanol, C_3F_7CH-$(OH)C_3F_7$, boils at 58° under 78 mm., and has d^{20}_4 1.6735; its refractive index at 20° is well below the scale of an Abbe refractometer (1.30); a sample sent to Minnesota Mining Co. was reported back as $n^{25}D$ 1.2911; its 3,5-dinitrobenzoate, melting at 84.0–84.2°, was analyzed. Calcd.: C, 29.9; H, 0.7; N, 5.0. Found: C, 30.2; H, 0.9; N, 5.6.

$C_3F_7CH(OH)C_3H_7$ boils at 63.5° under 45 mm., $n^{20}D$ 1.3391, was analyzed. Calcd.: C, 34.71; H, 3.72. Found: C, 34.18; H, 3.05. Its 3,5-dinitrobenzoate melts at 63.5–63.8°, and calcd.: N, 6.42. Found: N, 6.91.

The infrared spectra of the three alcohols were taken on the pure liquids at a cell thickness of 0.025 mm. with a Baird spectrophotometer. Each shows carbon–fluorine stretching in the range 7.1 to 10.0 μ. The carbon–hydrogen absorption at about 3.4 to 3.5 μ is in agreement with the assigned structures. For instance, in the case of C_3F_7CH-

(1) A. L. Henne and R. L. Pelley, This Journal, **74**, 1426 (1952).

(2) A. L. Henne and S. Richter, *ibid.*, **74**, 5420 (1952).

(3) E. T. McBee, W. F. Marzluff and O. R. Pierce, *ibid.*, **74**, 444 (1952).

(4) In agreement, Dr. R. N. Haszeldine reported at the September, 1952, Meeting of the A.C.S., the following values for perfluorinated alcohols: primary alcohols, 4×10^{-12}; secondary alcohols, 3×10^{-11}; tertiary alcohols, 3×10^{-10} for $(CF_3)_3COH$, 1×10^{-10} for $(C_3F_7)_3COH$.

(5) A. L. Henne and W. C. Francis, This Journal, **75**, 992 (1953).

(OH)C_3H_7 there is a strong, sharply defined band in this region with a transmittance of only 9%, while for the hydrogen-poorer $C_3F_7CH_2OH$ there is a much weaker absorption (42% transmittance) and the peaks of the band are less sharp; for $C_3F_7CH(OH)C_3F_7$ the carbon–hydrogen absorption is very weak, with 74% transmittance.

For $C_3F_7CH_2OH$ the strong, broad band for associated –OH is at 3 μ with 6% transmittance; it differs very little from that of 1-butanol. The unassociated –OH band appears only as a break in the curve at 2.8 μ with 69% transmittance.

For $C_3F_7CH(OH)C_3H_7$, the associated –OH band is very similar to that of $C_3F_7CH_2OH$, but with a slight shift toward shorter wave lengths at 2.97 μ with 10% transmittance. The reason for such a shift is not apparent, but might perhaps be attributed to steric factors. The non-associated –OH is still overlapped, and appears only as a break at 2.8 μ with 70% transmittance.

For $C_3F_7CH(OH)C_3F_7$ there is a strong difference. The non-associated –OH is now quite prominent at 2.8 μ with 39% transmittance; the associated –OH band is much less intense than in the previous cases, with 36% transmittance, and there is a shift to a shorter wave length at 2.9 μ. All this denotes a weaker hydrogen bonding, attributable to the reduced basicity of the hydroxylic oxygen atom.

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Reactions of Perfluorinated Propylmagnesium Iodide

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Pilot information on perfluorinated Grignard reagents, $C_nF_{2n+1}MgX$ has appeared recently,[1,2,3] and in a preliminary communication[1] we have shown that n-C_3F_7MgI could be formed and combined at low temperature with carbon dioxide or acetone in workable syntheses. The present paper reports further details and observed limitations in the formation and reactions of perfluorinated n-propylmagnesium iodide, C_3F_7MgI. The yields reported are not the best possible, but are either minimal yields or else clear indications that the reactions do not occur to any appreciable extent.

At room temperature, n-C_3F_7I reacts readily with magnesium in ethyl ether or tetrahydrofuran, but the main products are $CF_3CF=CF_2$ and fluorinated tars. Hydrolysis to C_3F_7H and titration with aqueous acids agree to show the presence of about 5% of C_3F_7MgI, and this order of magnitude can be confirmed by carbonation or condensation with acetone. The instability of n-C_3F_7MgI at this temperature is such that it is completely decomposed in a few hours.

(1) A. L. Henne and W. C. Francis, THIS JOURNAL, 73, 3518 (1951).
(2) R. N. Haszeldine, Nature, 167, 139 (1951); 168, 1028 (1951).
(3) R. N. Haszeldine, 120th and 122nd A.C.S. Meetings, September, 1951 and 1952.

At lowered temperatures, down to $-80°$, the stability of n-C_3F_7MgI improves progressively, but its rate of formation is much slower. As these two factors oppose each other, the problem of devising practical applications is not solved by a mere lowering of the temperature. As previously reported,[1] the best results were obtained by forming the Grignard reagent at low temperature in the presence of the compound with which it should condense. This procedure has now been applied to several derivatives with a carbonyl or carboxyl group.

The following results were noted when C_3F_7MgI was prepared at temperatures lower than $-40°$ and in the presence of the condensing agent which should consume it as made, except where otherwise stated: (1) Acetone gave a 10% yield of $C_3F_7C(OH)(CH_3)_2$, which was identified and measured as its dehydration product, $C_3F_7C(CH_3)=CH_2$. Mesityl oxide appeared as side-product, in quantities which varied with experimental conditions. (2) Butyraldehyde gave a 16% yield of the expected secondary alcohol, $C_3H_7CH(OH)C_3F_7$ and by-products attributed to aldol-type condensation of the aldehyde. (3) Perfluorinated butyraldehyde failed to give more than traces of the expected secondary alcohol, $C_3F_7CH(OH)C_3F_7$, and was recovered as aldehyde hydrate (38%), aldehyde polymer (48%) and perfluorobutyric acid (6%). (4) Ethyl formate gave a 24% yield of perfluorobutyraldehyde isolated as its hydrate, $C_3F_7CH(OH)_2$, but no secondary alcohol even when a large excess of the Grignard reagent was supplied. (5) Ethyl perfluorobutyrate gave 20% of perfluorinated ketone, $C_3F_7COC_3F_7$, but no tertiary alcohol. (6) Perfluorinated butyryl chloride, C_3F_7COCl, stopped the formation of the Grignard derivative. The condensation was therefore carried out in a separate step, which gave a 4% yield of ketone, $C_3F_7COC_3F_7$.

The reaction with a perfluorinated aldehyde, C_3F_7CHO, which could not suffer from competing aldolization but gave, nevertheless, practically no condensation with the Grignard reagent is consistent with the poor yields reported for its condensations with ordinary Grignard reagents.[4,5] With ethyl formate, the formation of C_3F_7CHO only agrees with the observed indifference of this aldehyde to C_3F_7MgI. With derivatives of the perfluorinated acids, the preferential formation of ketones is consistent with the action of ordinary Grignard reagents on these derivatives.[6]

The most practical result is the preparation of perfluorinated ketones from perfluorinated acids which are now commercially available.[7]

To illustrate, $C_3F_7COC_3F_7$ was synthesized from two moles of $C_3F_7CO_2H$, one mole of which was transformed into C_3F_7MgI by the sequence $C_3F_7CO_2H$ to $C_3F_7CO_2Ag$ to C_3F_7I to C_3F_7MgI, and

(4) E. T. McBee, J. F. Higgins and O. R. Pierce, THIS JOURNAL, 74, 1387 (1952).
(5) E. T. McBee, O. R. Pierce and J. F. Higgins, ibid., 74, 1737 (1952).
(6) K. N. Campbell, J. O. Knobloch and B. C. Campbell, ibid., 72, 4380 (1950).
(7) Minnesota Mining and Manufacturing Co., St. Paul, Minnesota.